

AD-A035 148

LITTON SYSTEMS INC MORRIS PLAINS N J AIRTRON DIV
PREPARATION OF RARE EARTH DOPED LASER MATERIALS AND ER, TM, HO:--ETC(U)
JAN 77 R F BELT, R UHRIN, L DRAFALL

N00014-76-C-0770
NL

UNCLASSIFIED

1 OF 1
AD-A
035 148



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

AD-A035 148

PREPARATION OF RARE EARTH DOPED LASER
MATERIALS AND Er , Tm , Ho : YLiF_4 LASER RODS

LITTON SYSTEMS, INCORPORATED
MORRIS PLAINS, NEW JERSEY

JANUARY 1977

ADA035148

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) PREPARATION OF RARE EARTH DOPED LASER MATERIALS AND Er, Tm, Ho: YLiF ₄ LASER RODS		5. TYPE OF REPORT & PERIOD COVERED Final Report Nov. 1, 1975 - Nov. 1, 1976
7. AUTHOR(s) R.F. Belt, R. Uhrin and L. Drafall		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Lambda/Airtron division Litton Systems, Inc. 200 E. Hanover Ave. Morris Plains, N. J. 07950		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0770
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Contract Administration Service 240 Route 22 Springfield, N. J. 07081		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research Department of the Navy 800 N. Quincy Street Arlington, Virginia 22217		12. REPORT DATE January 1977
		13. NUMBER OF PAGES iv + 23
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report)		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
<div style="border: 1px solid black; padding: 5px; text-align: center;"> DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited </div>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Laser crystals Yttrium lithium fluoride Holmium lasers Fluoride crystals		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This work describes two main activities in preparation of special materials for solid state lasers. The first portion is concerned with Ce ³⁺ , Eu ²⁺ , Yb ²⁺ and Pr ³⁺ doped hosts to examine possible lasing schemes in the green region based on d-f type lasing. Hosts were chosen with particular structures, coordination and charge to obtain band fluorescence centered near 5000 Å. The second portion was directed towards preparations of Er, Tm, Ho doped		

DD FORM 1473

EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

YLiF₄ to examine further the lasing at 2.06 μ m under Q-switching conditions. Ten new (3 x 30) mm laser rods were delivered to U. S. Army Electronics Command for testing. The compositions of these rods differed in the amount of Tm and Ho. Preparation of all fluoride compounds was from commercially available 5-9's purity oxides. Single crystal growth was achieved by top seeded solution in an HF atmosphere.

ia

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	ii
LIST OF FIGURES	iii
LIST OF TABLES	iv
1.0 INTRODUCTION	1
2.0 EXPERIMENTAL	3
3.0 RESULTS	6
3.1 Polycrystalline Preparations	6
3.2 Growth of YOF from a Flux	12
3.3 Growth of Er, Tm, Ho: YLiF ₄	14
4.0 CONCLUSIONS	22
5.0 REFERENCES	23

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	Avail. and/or SPECIAL
A	

DDC
 RECEIVED
 FEB 1 1977
 D

FOREWORD

This Final Report describes two related activities in materials preparation. One portion is directly concerned with a number of rare earth doped (Ce^{3+} , Eu^{2+} , Pr^{3+} , or Yb^{2+}) polycrystalline or single crystal compounds which may prove to be suitable for possible d-f lasing schemes. The other portion of the effort was directed towards the growth, laser rod fabrication, and testing of Er, Tm, Ho: YLiF_4 . The report describes all efforts under Contract No. N00014-76-C-0770 for the period November 1, 1975 to November 1, 1976. The contract work was under the coordination of Dr. Van O. Nicolai of the Office of Naval Research.

All compound preparation, single crystal growth, and laser rod fabrication were performed in the laboratories of Airtron Division of Litton Systems Inc., 200 E. Hanover Ave., Morris Plains, N. J. 07950. Dr. Roger F. Belt was the technical director of the project, Robert Uhrin and Dr. Larry Drafall were the principal engineers, and Karl Jensen was the senior technician. David Dentz, James Thomas, and Steven Turner performed all laser rod fabrication and quality testing. Active testing of laser rods was conducted at Fort Monmouth, N. J. by Vince Rosati. Fluorescent measurements on various preparations were reported by Prof. William Yen of University of Wisconsin.

The report was prepared by Roger F. Belt and released by the authors in December, 1976.

LIST OF FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	Absorption and luminescence of $\text{CaF}_2 + 0.1\%$ EuF_2 (Ref. 8)	9
2	Typical boule of $[100]$ grown Er, Tm, Ho: YLiF_4 (a) A typical boule polished on opposite faces (b)	19
3	Core drilled boules and rough blanks of Er, Tm Ho:YLF (a) Single crystal and rods of Er, Tm, Ho:YLF (b)	21

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
I	Summary of Polycrystalline Preparations	10
II	Summary of Spectroscopic Properties	13
III	Suggested Compositions for Growth of YLF at Start of Program	15
IV	Single Crystals of YLiF_4	16
IV	Continued	17

1.0 INTRODUCTION

All of the well known solid state crystal lasers based on trivalent rare earth ions operate on weak forbidden $4f \rightarrow 4f$ transitions for optical emission and absorption. In recent years more attention has been given to a possible new scheme for laser action which uses very intense allowed inter-configuration $4f \rightarrow 5d$ transitions. The excited $4f^{n-1}5d$ bands for most of the rare earth ions are at energies above 50000 cm^{-1} (6.2 eV). Therefore in some single crystals or glasses the fundamental band absorption of the host may prevent fluorescence from 5d bands. In other cases 5d excitation may be quenched by non-radiative decay to overlapping levels of the ground $4f^n$ configuration. However there are important exceptions. The energy level structure of an ion may be one where there are no 4f levels to quench 5d bands. This occurs in certain ions such as Ce^{3+} , Eu^{2+} , Yb^{2+} and a few other ions.

Work in several laboratories has been directed towards examining spectra and designing materials which may give 5d-4f type lasing. This class of laser has several advantages. Among these are broad optical pump bands centered in the near uv, possible four level operation at 25°C , band emission in the visible, tunability over several hundred \AA , and high quantum efficiency. Such a laser is a solid state analog of a dye laser. By appropriate choices of rare earth ion and host, oscillation wavelengths may be adjusted for specific applications in laser technology.

While the spectra, laser scheme, and possible materials have been studied in some systems, apparently no working laser has been developed yet. The reasons for this are many but a greater understanding of allowed transitions of 4f impurity ion systems in crystalline environments is essential as a start. These studies include the structure of the host, the effect of different coordination about the impurity ion, and symmetry effects. Some of the rough data can be collected from an examination of polycrystalline material but a single crystal is more helpful if it is available. Further simplification of emission and absorption in 5d - 4f systems may be obtained by examining a system such as Ce^{3+} with a single 4f electron. An initial study of Ce^{3+} in $\text{Y}_3\text{Al}_5\text{O}_{12}$ was made [1] and further hosts were reported later [2]. Some operating principles were determined but even for Ce^{3+} the spectra are not predictable.

The purpose of the Airtron portion of this program involved the preparation of several polycrystalline hosts doped with ions such as Ce^{3+} , Er^{2+} , or Yb^{2+} which may lead to 5d band fluorescence centered around 4800 - 5000 Å. Once a satisfactory polycrystalline material is obtained, an effort would be made to get single crystals for testing laser action. Most of the anticipated compounds are oxides, fluorides, or oxyfluorides which could be readily prepared if needed in fairly large polished pieces.

The remaining portion of our research effort was devoted to laser rod fabrication of Er, Tm and Ho doped YLiF_4 .

This material and its preparation have been studied by us in the past [3]. Satisfactory laser action at $2.06\text{ }\mu\text{m}$ has been obtained but two problems remained. One was related to the proper amounts of dopants and the other to trace impurities which may lead to damage upon Q-switching. The dopant level was examined in a series of crystal growth runs where the Er was fixed and Tm/Ho was varied at a constant ratio. The trace impurity problem was examined by using the highest purity oxides available before conversion to fluorides. In the past considerable difficulty was experienced in the core-drilling of rough diameter laser rods. These problems essentially have been solved and we now obtain several usable (3×30) mm rods per growth run.

2.0 EXPERIMENTAL

Experimental preparations were formulated by us and consisted of two main types, polycrystalline ceramic sintered powders and single crystals of substituted YLiF_4 . The first of these were prepared from reagent grade or better quality oxides, carbonates, or nitrates. The required components were weighed on a balance, mixed at room temperature, and heated in either a platinum or an iridium crucible. The latter were used as a susceptor in an RF coil operated at 450 KHz. The temperature of sintering was checked with an optical pyrometer which was calibrated against pure oxides of known melting points. For many of the preparations some form of atmosphere control was essential. This was achieved by

enclosing the crucible, its insulation, and the coil in either a quartz or glass container. Gases of O_2 , N_2 , A, or a N_2-H_2 mixture were passed into the bell jar at the bottom and exhausted at the top. The atmosphere was maintained during the entire sintering cycle. Dopants of selected rare earth elements were added in the form of 99.99% oxides and concentration levels were usually 1 atomic per cent substitutions.

Several growth runs were attempted from high temperature fluxes. In these runs the components were added to a 3 inch diameter x 3 inch high platinum crucible. Either a crimped or welded lid formed the closure. The crucible was placed on an Al_2O_3 pedestal and elevated into the hot zone of a resistively heated Globar-element cylindrical furnace. The furnace was heated to 1000-1250°C and then a programmed cooling rate of 1-2°C/hr was maintained until the crucible reached 900-950°C. At this temperature the flux was poured after lid removal. In other cases the flux was then cooled to 25°C, the welded lid removed, and the crystals separated by acid leaching of the flux.

Preparations of $Y_{1-x-y-z}Er_xTm_yHo_zLiF_4$ were developed from 99.99% purity oxides of Y, Er, Ho, and Tm which were converted to fluorides and LiF. The oxides were obtained as polycrystalline powders from Research Chemical Corp. and the LiF was purchased as single crystal ultraviolet grade material from Harshaw Chemical Co., Analyses of all components have been given in our previous reports. One deviation was made in

our current work wherein several growth runs were prepared from 5-9's starting oxides. The latter were the highest purity obtainable in any rare earth compound.

All compositions were begun with individual mixtures of the component oxides. Our procedure utilized about 150 g of mixed oxides which were converted subsequently to fluorides by means of a high temperature platinum hydrofluorination apparatus. Final temperatures were raised to 1200°C for all the fluorides. This temperature is above the melting point of each of the component fluorides. As a result a very homogeneous mixed crystal of mm size particles is obtained. The polycrystalline mass can be stored with little chance of further hydrolysis.

Single crystals of substituted YLiF_4 were grown by means of the top-seeded solution method [4]. A platinum growth furnace and crucible were utilized to maintain growth under a flowing atmosphere of 90% N_2 -10% HF. A weight sensing diameter control system which performed a continuous weighing of the seed gave excellent results on the crystal shape. Starting compositions were 47 mole % rare earth fluorides and 53 mole% LiF. The crucible size was 1.5 inch diameter x 1.5 inch high. It was filled to 90% of its capacity at the growth temperature. All boules were [100] or a-axis oriented along the growth direction. The pull rate and rotation rate were varied to control the solid-liquid interface shape. The latter was flat in most cases. When several runs of one

composition were made, the melt was replenished with no decrease of crystal quality. If a composition was changed the crucible was cleaned throughly between runs. The greatest asset to a clear defect-free single crystal was a proper heating and homogeneous solution before growth was attempted. A high pull rate also tended to give small bubbles concentrated along the growth interface. Most of our crystals were grown at 0.6 mm/hr and 20 rpm. The boules were about 2 cm in diameter x 5-6 cm long. There appears to be no difficulties in going to larger sizes if these are needed for increased yields. From the 2 cm diameter boules at least two and sometimes four (3 x 30) mm laser rods could be core drilled in rough form.

3.0 RESULTS

The results of our materials preparation can be classified into two main parts. The first of these is concerned with polycrystalline compounds which were chosen mainly for examination of their fluorescent properties after doping with particular rare earth ions. The second portion of our work is concerned solely with the LiYF_4 laser compositions.

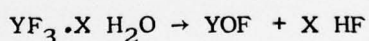
3.1 Polycrystalline Preparations

At the beginning of our work it was thought that compounds containing rare earths in a coordination of 6 oxygen or 8 (oxygen and fluorine) may be suitable for examination. YOF is such a material and it is reported to have several crystal structures which depend on the particular stoichimetry of the preparation. Ideally the rare earth oxyfluorides form cubic fluorite CaF_2

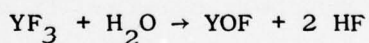
phases where the rare earth is surrounded by eight (F + O) at the corners of a cube and each F + O is surrounded by a tetrahedron of rare earths [5]. Distortions of the cubic structure occur to give a tetragonal phase over the excess fluorine composition range MOF_3-2n ($0.7 < n < 1.0$) where M is a rare earth. At the stoichiometric composition MOF a further rhombohedral structure results from instability of the tetragonal phase. The rhombohedral phase of YOF has Y-4F distances of 2.28 \AA and Y-4O distances of 2.44 \AA . All structural data have been determined from x-ray powder diffraction patterns since no single crystals were available.

The crystal structure of YOF is closely related to composition and therefore to the exact mode of preparation. In general the oxyfluorides can be prepared by three different methods:

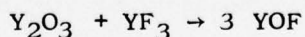
- (1) Decomposition of trifluoride hydrates



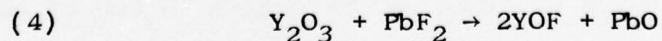
- (2) Hydrolysis of trifluorides in moist air



- (3) By heating an oxide and fluoride



An alternate method based on the presence of YOF in fluxed melts of PbO , PbF_2 and Y_2O_3 is also worthwhile for small single crystals.



It should be noted that in the case of the phase diagram of the $\text{YF}_3 - \text{Y}_2\text{O}_3$ system very little is known. Logically this

should be the first experimental area to be investigated. It should be possible to grow single crystals if the composition is fixed and specific compositions may be congruently melting. Some atmosphere control may also be required in the form of H_2O and HF. Most preparations of the oxyfluorides have been attempted in polycrystalline form and some have been examined as infrared - to visible conversion phosphors [6,7]. Figure 1 gives an example of Eu^{2+} : CaF_2 absorption and fluorescence. The presence of some oxygen in the immediate neighbors of the Eu^{2+} may shift the fluorescent emission closer to $0.48 \mu m$ since Ce^{3+} fluorescence in oxygen based hosts is shifted from the UV to the visible.

As a preliminary tool for the preparation and optical examination of doped YOF, we prepared mixtures of YF_3 and Y_2O_3 in fixed compositions after equation [3] above. Each of these mixtures was doped with 1% Ce^{3+} in the form of CeF_3 . The exact compositions are listed in Table I. Preparations were made by mixing all components thoroughly, then heating to $1200^\circ C$, and finally to $1600^\circ C$. All sintering runs were performed in an atmosphere of air. It was found that YOF was definitely formed and checked by x-ray diffraction phase analysis. However no melting of YOF occurred up to the melting point of Pt ($1780^\circ C$). The effects of composition were minor as given in Runs 1A, 1B, 1C. Run 2 was prepared as a 50-50 composition of YF_3 and Y_2O_3 plus 1% CeF_3 . The material was placed in an iridium crucible and RF heated in one of our growth stations to about $2000^\circ C$. A N_2 atmosphere was used. Material at the bottom of the crucible showed some sign of melting but the top

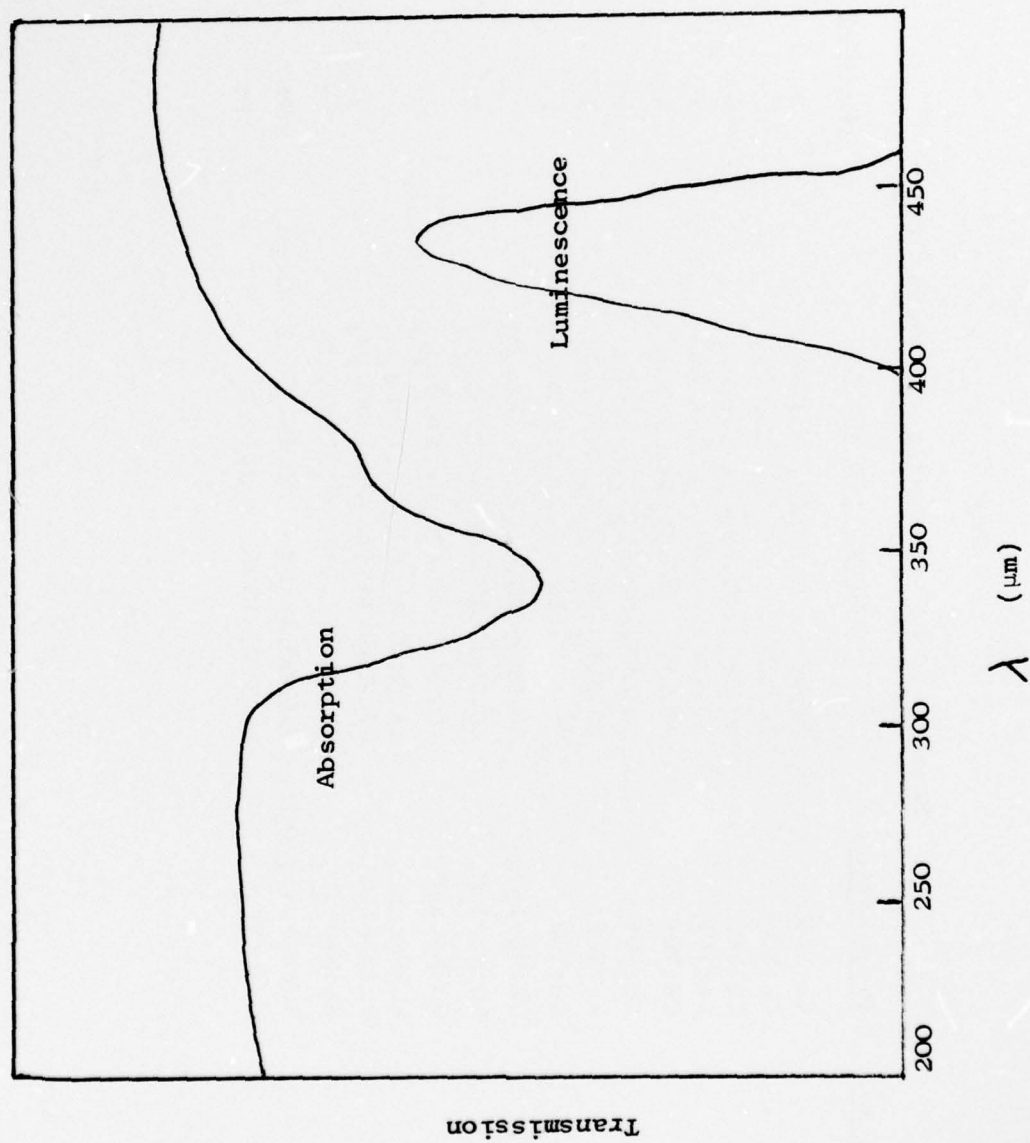


Figure 1. Absorption and luminescence of $\text{CaF}_2 + 0.1\% \text{EuF}_2$ (Ref. 8)

TABLE I
Summary of Polycrystalline Preparations

<u>Run No.</u>	<u>Preparation</u>	<u>Composition (Wt.%)</u>	<u>Crucible</u>	<u>Ambient Gas</u>
1A	Ce:YOF	38.4YF ₃ , 60.6Y ₂ O ₃ , 1.1CeF ₃	Pt	Air
1B	Ce:YOF	29.3YF ₃ , 69.7Y ₂ O ₃ , 1.0CeF ₃	Pt	Air
1C	Ce:YOF	48.3YF ₃ , 50.6Y ₂ O ₃ , 1.1CeF ₃	Pt	Air
2	Ce:YOF	38.4YF ₃ , 60.6Y ₂ O ₃ , 1.1 CeF ₃	Ir	N ₂
3A	Ce:YOF	38.0YF ₃ , 60.5Y ₂ O ₃ , 1.5CeF ₃	Ir	N ₂ -H ₂
3A1	Ce:YOF	38.0YF ₃ , 60.5Y ₂ O ₃ , 1.5CeF ₃	Pt	N ₂ -H ₂
3B	Eu:YOF	38.8YF ₃ , 58.4Y ₂ O ₃ , 2.7Eu ₂ O ₃	Ir	N ₂ -H ₂
3B1	Eu:YOF	38.8YF ₃ , 58.4Y ₂ O ₃ , 2.7 Eu ₂ O ₃	Pt	N ₂ -H ₂
3C	Eu:MgAl ₂ O ₄	26.9MgO, 70.4Al ₂ O ₃ , 2.7Eu ₂ O ₃	Ir	N ₂ -H ₂
3C1	Eu:MgAl ₂ O ₄	26.9MgO, 70.4Al ₂ O ₃ , 2.7Eu ₂ O ₃	Pt	N ₂ -H ₂
3D	Eu:MgGa ₂ O ₄	16.8MgO, 81.6Ga ₂ O ₃ , 1.6Eu ₂ O ₃	Ir	N ₂ -H ₂
3D1	Eu:MgGa ₂ O ₄	16.8MgO, 81.6Ga ₂ O ₃ , 1.6Eu ₂ O ₃	Pt	N ₂ -H ₂
3E	Eu:BaAl ₂ O ₄	57.2BaO, 41.3Al ₂ O ₃ , 1.5Eu ₂ O ₃	Ir	N ₂ -H ₂
3E1	Eu:BaAl ₂ O ₄	57.2BaO, 41.3Al ₂ O ₃ , 1.5Eu ₂ O ₃	Pt	N ₂ -H ₂
4	Eu:SrMgAl ₁₀ O ₁₇	5.8MgO, 19.6BaO, 72.19Al ₂ O ₃ , 1.7Eu ₂ O ₃	Pt	N ₂ -H ₂
5	Ce:LiYF ₄	82.7YF ₃ , 15.0LiF, 2.3CeF ₃	Pt	HF-N ₂ -H ₂

showed only a sintering. The presence of YOF was confirmed in both parts of the crucible.

The series of runs in 3A and B were performed with the object of placing as much Ce^{3+} or Eu^{2+} in the sintered mixture as possible. To this end a reducing atmosphere of forming gas (85% N_2 - 15% H_2) was used in two stages. The first sintering of YOF was carried out rapidly in an iridium crucible over a period of 8 - 12 hours. Heating was up to 1400-1500°C. At the end of this treatment the material was removed from the crucible and ground. It was then placed in a platinum crucible and heated to 1200°C for 14 hours in a N_2 - H_2 atmosphere.

The runs 3C, 3D, and 3E were all based on spinel or hexagonal type structures where the rare earth may likely be incorporated with a 6 coordination. The preparations were again made in two stages utilizing a N_2 - H_2 atmosphere. The dopant was primarily Eu. Run 4 was based on some previously reported [9] results with hexagonal aluminates which gave favorable results. Run 5 was a polycrystalline melt of LiYF_4 doped with CeF_3 and prepared in HF - N_2 - H_2 . If the Ce^{3+} substitutes for Y in this tetragonal scheelite structure compound, then the coordination is eight F^- . Thus the surroundings would be the other end member of the series 8F^- , $4\text{O}^{2-} + 4\text{F}^-$, and 8O^{2-} in terms of ligand charge. It is strongly believed that a proper coordination and charge arrangement will place the Ce^{3+} fluorescence close to 5000Å.

Table II is a summary of some of the spectroscopic

properties of our polycrystalline materials. These data were obtained by courtesy of Prof. W. C. Yen of the University of Wisconsin. Special apparatus was constructed for the examination of these powders. While most of the Eu^{2+} doped compounds gave some fluorescence, there appeared to be difficulty in the properties of the Ce^{3+} . Some of this may be due to the mode of preparation or the amount of Ce^{3+} obtained in a structure such as YOF. More trials will be made in the future on YOF and on other host structures. Obviously if single crystals can be grown this may favor the situation.

3.2 Growth of YOF from a Flux

The single crystal growth of YOF appears to be a rather difficult problem because of composition, phase relations in melts, and size requirements. During the development of PbO-PbF_2 fluxes for the growth of YIG, it was noticed that small crystallites of YOF appeared as an impurity [10]. Obviously the reaction of some Y_2O_3 with F^- occurred and melts rich in Y_2O_3 favored the formation of YOF. In 1968 some deliberate attempts were made to prepare a series of rare earth oxyfluorides [11]. These attempts were all based on the crystallization of R_2O_3 from $\text{PbF}_2 - \text{PbO}$ melts. In most cases the results gave small crystals of both R_2O_3 and ROF phases. The latter were of small cube or plate morphology and mm size.

We have attempted the growth of YOF by using the slow cooling method of Garton. The Y_2O_3 was dissolved in $\text{PbF}_2 - \text{PbO}$ at $1200 - 1300^\circ\text{C}$ and the platinum container was cooled to 950°C at a rate of $2-3^\circ/\text{hr}$. At the end of several days of

Table II

Summary of Spectroscopic Properties *

Run No.	Material	Nature & Peak Fluorescence	Linewidth (\AA)	Lifetime (μs)	Relative Intensity
1A	Ce ³⁺ :YOF	None	None	—	—
1B	Ce ³⁺ :YOF	None	None	—	—
1C	Ce ³⁺ :YOF	None	None	—	—
2	Ce ³⁺ :YOF	None	None	—	—
3A	Ce ³⁺ :YOF	None	None	—	—
3A1	Ce ³⁺ :YOF	None	None	—	—
3B	Eu ²⁺ :YOF	Red	Line	—	—
3B1	Eu ²⁺ :YOF	Red	Line	—	—
3C	Eu ²⁺ :MgAl ₂ O ₄	None	None	—	—
3C1	Eu ²⁺ :MgAl ₂ O ₄	Band, 4700	1000	1.3	4
3D	Eu ²⁺ :MgGa ₂ O ₄	Red	Line	—	—
3D1	Eu ²⁺ :MgGa ₂ O ₄	None	None	—	—
3E	Eu ²⁺ :MgAl ₂ O ₄	Band, 5000	1000	1.0	9
3E1	Eu ²⁺ :BaAl ₂ O ₄	Band, 5000	1000	1.2	19
4	Eu ²⁺ :SrMgAl ₁₀ O ₁₇	Band, 4900	1000	1.8	11

* Data provided by Prof. W. C. Yen, U. of Wisconsin

crystallization the flux was cooled to 25°C and the remaining flux removed by acid leaching. The formation of YOF occurred but only as a finely divided powder and not as single crystals. Several other attempts were made with no greater success. The size of our crucibles was much larger than the 50ml ones originally used by Garton. This may have contributed to a lessened evaporation of solvent and a tendency not to crystallize over the similar time period of cooling. More trials should be made by using alternate procedures.

3.3 Growth of Er, Tm, Ho: YLiF₄

Under this year's program we have also continued the growth of single crystals of Er, Tm, Ho doped YLiF. The main purpose of this work was to provide (3 x 30) mm laser rods of suitable compositions and quantity for Q-switch laser testing. Some of the more desirable compositions suggested for growth are listed in Table III. The Pr doped system was grown for an entirely different purpose. The reasons for the compositional changes are based partially upon previous tests conducted at the U. S. Army Electronics Command and partially upon compositions grown or suggested by alternate workers [12,13]. The energy transfer mechanism in this quasi four level system is not known for certain and some latitude is suggested in the Tm and Ho concentration for efficient Q-switching at 25°C.

A summary of all single crystal growth runs is given in Table IV. Most of these runs were solution grown using a composition of 51 - 53 mole % LiF and the remainder rare earth trifluoride. Two exceptions were made in runs 48 and 69

Table III

Suggested Compositions for Growth of YLF
at Start of Program

Composition No.	Mole %					$\frac{Tm}{Ho}$	$\frac{Pr}{Ho}$
	\underline{Y}	\underline{Er}	\underline{Tm}	\underline{Ho}	\underline{Pr}		
1	33.2	50	16	0.8		20	
2	33.0	50	16	1.0		16	
3	32.5	50	16	1.5		10.7	
4	44.75	50	5.0	0.25		20	
5	47.9	50	2.0	0.1		20	
6	47.8	50	2.0	0.2		10	
7	99.5	0	0	0		0	.5
8	39.5	50	10	.5		20	
9	42.96	50	6.7	.34		19.7	

Table IV
Single Crystals of YLiF_4

Run No.	Composition (Mole %)			Pull Rate (mm/hr)	Rot. (rpm)	Diam. (mm)	Length (cm)	Remarks
	Y	Er	Tm	Ho				
48	100	--	--	--	32	16	5.8	Stoichiometric composition tried. No crystal grown; melt adjusted to 53 mole% LiF, good growth.
49	100	--	--	--	30	2π	6.5	Large diameter test run, crystal good.
50	33.0	50	16	1.0	20	19	6	Good growth control, longer interface, no scattering. Seven rods fabricated.
51	39.5	50	10	0.50	20	19	6	Scattering present, excess LiF used to eliminate scattering. Scattering remained.
52	42.95	50	6.7	0.34	20	20	6	15 mm band of scattering in straight portion of boule.
53	39.5	50	10	0.50	20	19	6.3	Scattering in top section of boule. Bottom 18mm scatter-free.
54	42.96	50	6.7	0.34	20	19.5	6	Top 10 mm and bottom 16mm scatter-free. Center portion had scattering present.
55	39.5	50	10.0	0.50	20	19	6	Boule contained scattering as in Run No, 54.
56A	99.8	--	--	.02	20	19	5.0	No haze or scattering, crystal clear under fluorescent light, pale green fluorescence under incandescent light.
56B	99.0	--	--	1.0	20	19	5.0	No haze or scattering, crystal pinkish under fluorescent light, green fluorescence under incandescent light.
57	42.96	50	6.7	0.34	20	18	5.0	Same haze and scattering pattern as in Run No. 54.

Table IV (Continued)

Run No.	Y	Ex	Im	Ho	Pull Rate (mm/hr)	Rot. (rpm)	Diam. (mm)	Length (cm)	Remarks
58	39.5	50	10.0	0.50	.63	20	16	7.5	Scattering closer to bottom of boule. Four rods fabricated.
59	42.96	50	6.7	0.34	.63	20	17	7.7	Scattering near bottom of boule. Top 30mm and bottom 10mm appear scatter-free.
60	42.96	50	6.7	0.34	.63	20	18	7.5	Same as No. 59. Six rods fabricated.
61	42.96	50	6.7	0.34	.63	20	18	7.2	Same as no. 59.
62	33.0	50	16	1.0	.63	20	18	7.2	Approximately same as No. 59.
63	42.96	50	6.7	0.34	.63	20	18	7.2	Boule appears haze and scatter-free. One 30mm rod fabricated.
64	39.5	50	10	0.50	.63	20	16	8.0	No scattering or haze.
65	42.96	50	6.7	0.34	.63	20	17	7.2	No scattering or haze.
66	99.0	--	--	--	.63	20	18	6.0	Special dopant 1% NiF_2 . Entire boule contained scattering.
67	99.0	--	--	--	.63	20	18	5.4	Special dopant 1% NiF_2 . Entire boule contained scattering. HF flow stopped during run.
68	99.0	--	--	--	.63	20	18	8.2	Special dopant 1% NiF_2 . Oscillations in diameter control, scatter-free except below diameter change, light green fluorescence.
69	33.0	50	16	1.0	.63	20	17	8.2	Stoichiometric composition would not grow. Excess (LiF) added, successful growth.

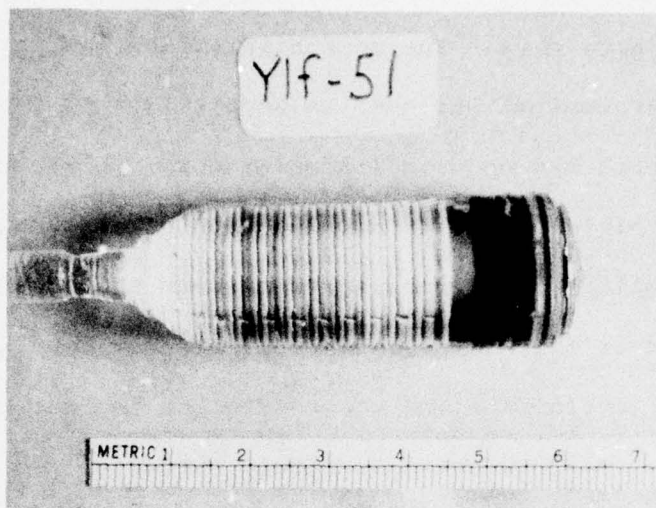
where a stoichiometric melt was compounded and growth was attempted from this pure melt. The pure melt gave a crystal of poor quality and growth was difficult to commence. Upon the addition of 1 - 2% LiF, regular growth became possible from solution. Thus it appears that in an N_2 - HF atmosphere the matter of a congruently melting compound may still be undecisive. However we have not pursued vigorously the growth from pure melts and thermal conditions may not be optimized. From a practical position all of our compositions which yielded laser rods were grown from solution.

In the remarks column of Table IV several boules contained small sections which had visible scattering sites. The scattering sites or haze was evident when the boule was probed laterally or longitudinally with a collimated beam of light or a laser. Boules with haze usually contained the defects in the middle and not at the start or finish of the growth run. Thus our best guess was that the haze was associated with the solution properties of the system and temperature control. Haze was totally eliminated by using a long soak period for all components before growth commenced. All of the boules from which laser rods were obtained were grown free of haze along the entire length. Thus the problem of damage in Q-switching is not thought to be associated with any visible scattering centers prior to lasing.

Some typical results of boule growth are given in Fig. 2(a).

All boules were grown along an [100] or a-axis. Slow growth of 0.6 mm/hr gave excellent quality and a complete run required

(a)



(b)



Fig. 2 (a) Typical Boule of [100] grown Er, Tm, Ho : YLiF_4

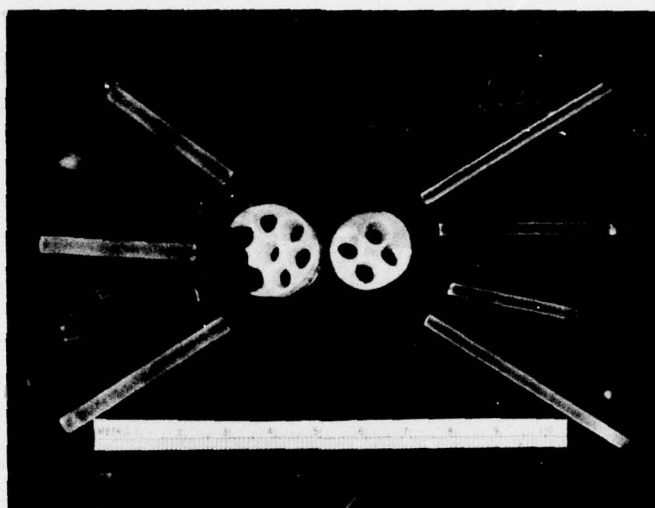
(b) A typical boule polished on opposite faces

about three days. The growth interface was slightly convex and diameter control was good to about $\pm 2 - 3\%$. Fig. 2(b) was taken with two opposing faces window - polished. The crystal was completely free of any interior defects when grown properly. The quality is generally reflected in the interferometer pattern of the boule or fabricated rods. Any areas of cores, strain, inclusions, or other interior regions of different refractive index are immediately evident.

One persistent problem has been associated with the Er, Tm, Ho doped compositions. This is related to the fabrication procedure and the mechanical properties of the boules. For all pure YLiF_4 or crystals doped with 1% of a single element, the boules are very stable, can be cut easily, and rods can be core drilled readily. However the Er, Tm Ho doped boules appear to be more brittle and fracture frequently during core drilling. Obviously the properties are different when the same tools and procedures are used for similar boule quality. In spite of these differences most of boules have yielded 2, 4, 6 and sometimes 8 rods of (3 x 30)mm size. Fig. 3 (a) shows some core drilled boules in the center with (3 x 30) or (3 x 50) mm rough blanks situated on either side. Fig. 3 (b) illustrates a grown boule and finished laser rods. Notice in Fig. 3 (a) that a rod was extracted from the center of the boule. This rod was of comparable quality to all others taken from other sections of the boule. This is indicative of low strains across the nearly flat growth interface.

Several other singly doped crystals of YLiF_4 were prepared

(a)



(b)

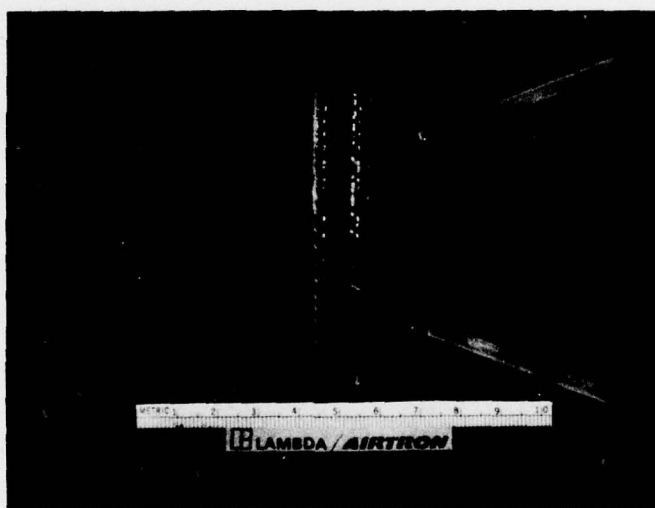


Fig. 3 (a) Core drilled boules and rough blanks of Er, Tm, Ho:YLF.

(b) Single crystal and rods of Er, Tm, Ho:YLF.

for a number of purposes. These included Pr to try to obtain lasing in the green, Ho for examination of spectroscopy, and Ni^{2+} for examination of absorption spectra. Some of these materials were optically fabricated into prisms, discs, or other shapes for particular experiments.

4.0 CONCLUSIONS

Preparation of Ce^{3+} and Eu^{2+} doped materials showed complicated d-f transitions which move the band type fluorescence. The presence of fluorescence from Ce^{3+} appears to be sensitive to the particular structure, coordination, charge effects, and mode of preparation. Eu^{2+} readily fluoresced but this multi-4f electron system is complicated to explain. YOF is considered an ideal host for Ce^{3+} but no fluorescence was observed. Single crystals even in mm size are difficult to grow.

Additional preparations of Er, Tm, Ho doped YLiF_4 were made in single crystal form to provide (3 x 30) mm laser rods. Ten new rods were prepared and delivered for testing. The boule growth and rod fabrication have now been developed into a routine operation. Single doped compositions of YLiF_4 are easy to fabricate but some problems may occur with very high levels of Er and Tm.

5.0 REFERENCES

- [1] G. Blasse and A. Bril, Appl. Phys. Letters 11, 53 (1967).
- [2] G. Blasse and A. Bril, J. Chem. Phys. 47, 5139 (1967).
- [3] R. Uhrin and R. F. Belt, Summary Report, Contract No. N00014-70-C-0379 Jan. 1976.
- [4] V. Belruss, T. Kalnajs and A. Linz, Mat. Res. Bull. 6, 899 (1971).
- [5] For a discussion of various fluorite type oxyfluorides see A. F. Wells, "Structural Inorganic Chemistry" (Oxford, London, 1962); P. 388, R.W. G. Wyckoff, "Crystal Structures", Vol.II, (Interscience, New York, 1965) p. 52; D. Brown, "Halides of the Lanthanides and Actinides", (Wiley-Interscience, New York, 1968) pp. 99-100.
- [6] J. Wojciechowski, I. Pawelska, R. Grodecki and L. Symanski, J. Electrochem. Soc. 122, 312 (1975).
- [7] T. Matsubara, Japan J. Appl. Phys., 10, 1647 (1971).
- [8] R. Leckebusch, A. Neuhaus, and R. Recker, J. Crystal Growth, 16, 10 (1972).
- [9] A.L.N. Stevels and A.D.M. Schrama-de Pauw, J. Electrochem. Soc. 123, 691 (1976).
- [10] J.W. Nielsen, J. Appl. Phys. 31, 51s (1960).
- [11] G. Garton and B.M. Wanklyn, J. Mat. Science 3, 395 (1968).
- [12] E.P. Chicklis, R.C. Folweiler, C.S. Naiman, A. Linz, H.P. Jenssen, and D.R. Gabbe, TR ECOM - 0013-F, January, 1973. TR ECOM - 0066-F, October, 1974.
- [13] D.P. Devor, R.C. Pastor, M. Robinson, W.M. Akutagawa, K. Arita, TR ECOM - 0034-F, November, 1974.